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MEMORANDUM FOR PRR (~~Contractor~~/In-House Publication)

FROM: PROI (TI) (STINFO) 27 May 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0118
Sheehy, "HEDM Research at AFRL: Perspectives, Progress, and Directions"
Presentation at HEDM Conference **(Public Release)**

HEDM Research at AFRL:
Perspectives, Progress, & Directions

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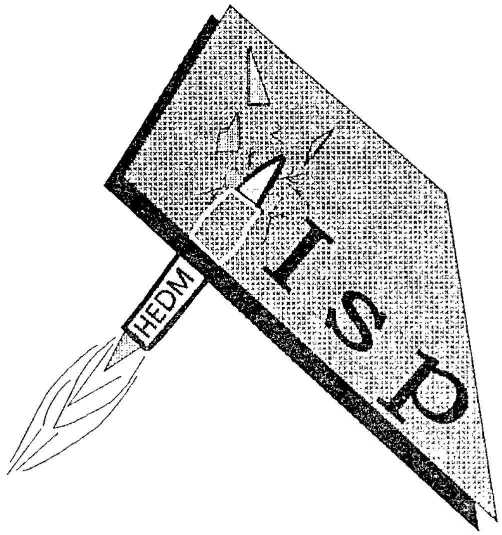
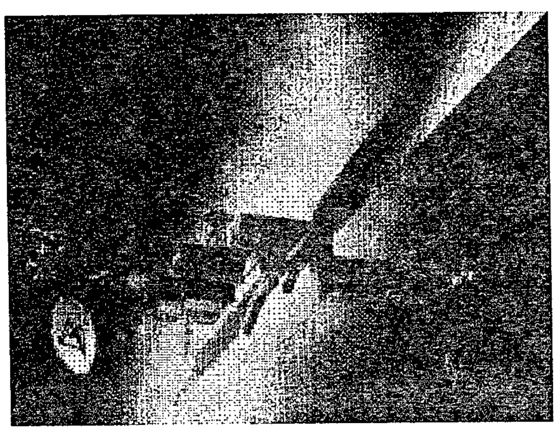
HEDM Program Objective

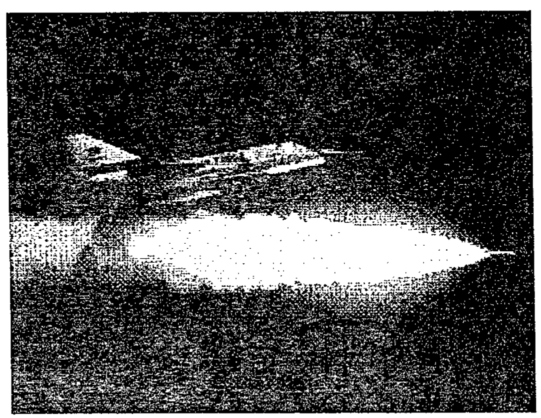


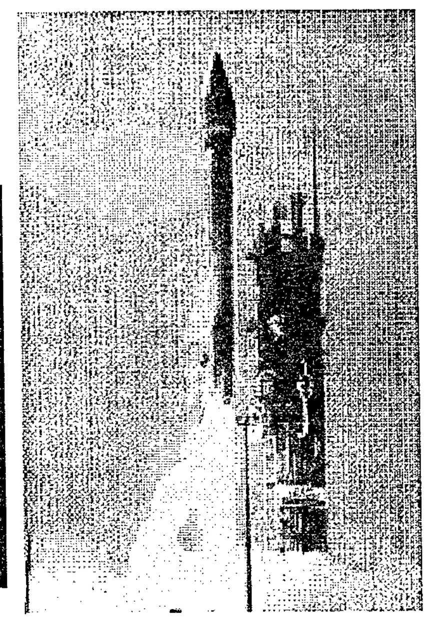
Breaking the performance barrier

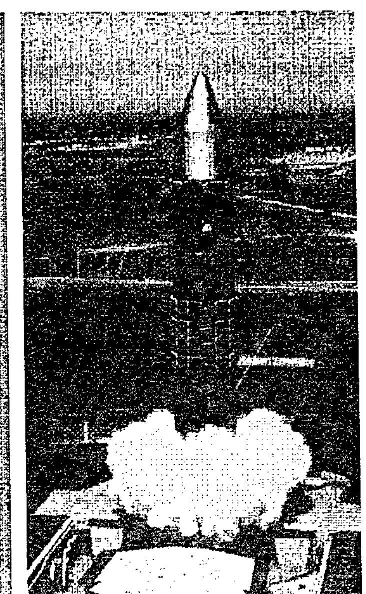
Identify and develop advanced chemical propellants for rocket propulsion applications

- Hydrocarbons for liquid boosters
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for satellite propulsion
- Cryogenic propellants for upper stages

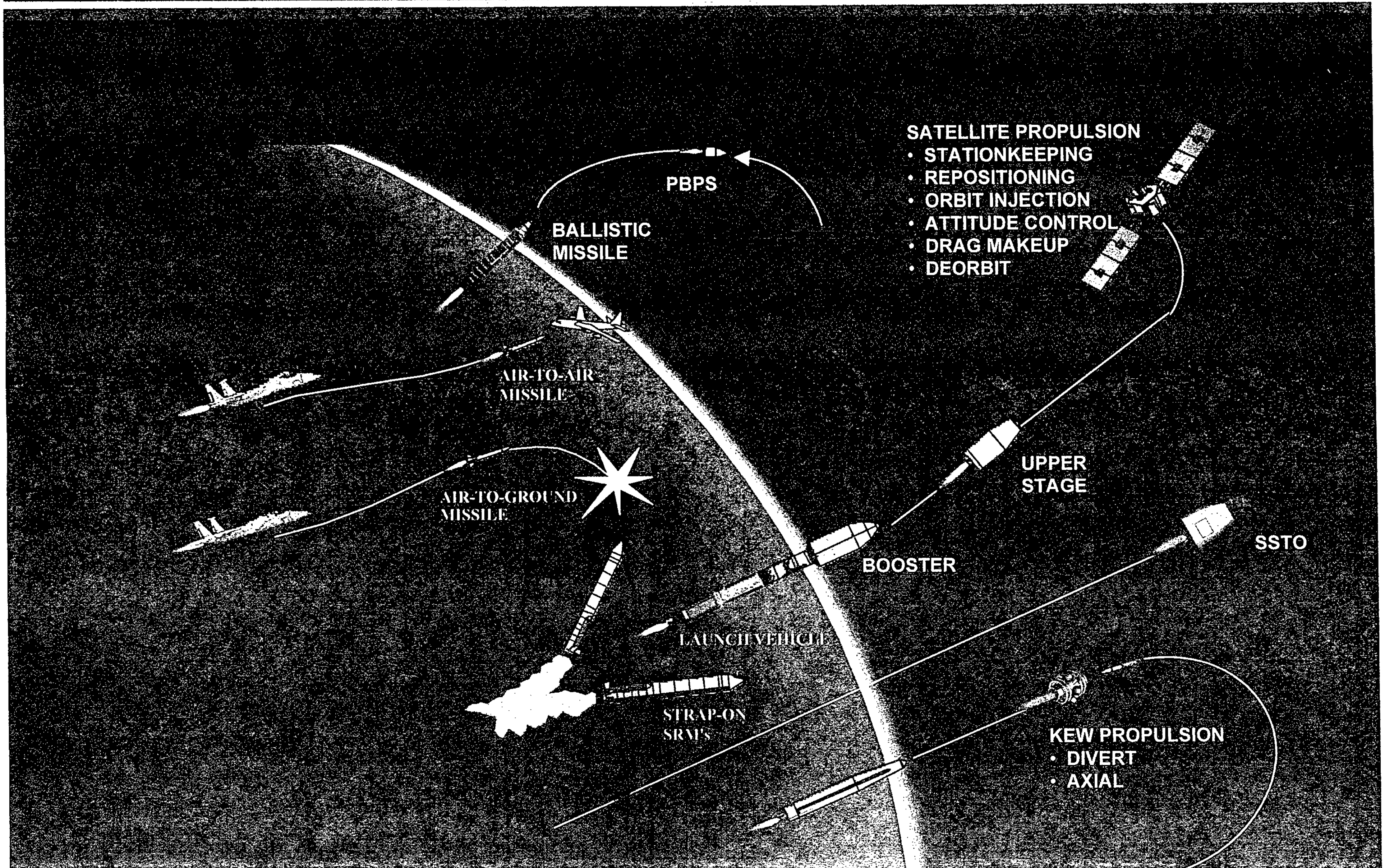








Propulsion Needs for Air Force Missions



HEDM Program Motivations

The performance limits of current propellants have been reached

- The constituents of current propellants have been known for decades
- New missions require higher-performing propulsion systems

A revolutionary propulsion source would substantially improve our ability to access and exploit space

- Fusion, antimatter, and beamed energy are tantalizing but distant
- Chemical propulsion will remain the method of choice for many applications
- Novel chemical propellants offer great potential for near-term improvements

Challenges to Developing HEDM Propellants

Materials with high energy densities are frequently thermally unstable or extremely shock sensitive

Synthesis and characterization methods for many novel forms of energetic materials are unknown

The methods used to synthesize new energetic materials can be difficult to scale up

Payoffs of HEDM Propellants

- Larger payloads, smaller vehicles, and lower launch costs
- Improved capability to access and exploit space

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas G/ Centaur D-1A	RP-1/LOX (Isp = 295 s)/ LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 (+25%)
SSTO RLV	Rockwell SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 (+70%)
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 (+49%)

HEDM research at AFRL is aimed at increasing propellant Isp by 5 to 50%

HEDM Program Motivations

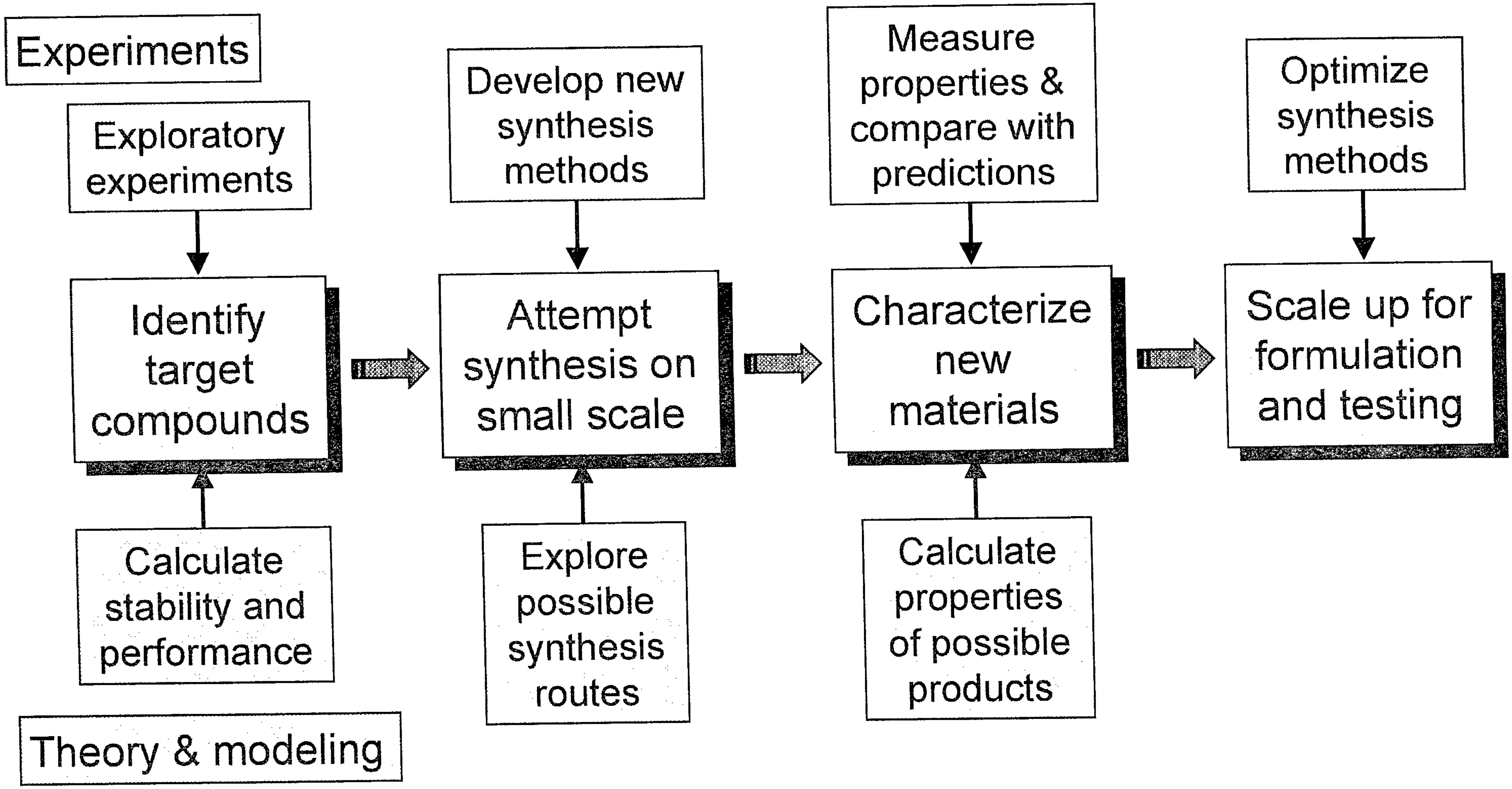
"The highest leverage technology area impacting launch vehicles is the development of high-energy-density materials for use as propellants."
-- New World Vistas Panel on Space Technology (1995)

"The launch community will continue to rely on chemical rocket propulsion for the foreseeable future. Technology breakthroughs in propellant performance, density, and affordability will be crucial." -- Breakthrough Technologies to Meet Future Air and Space Transportation Needs and Goals (NAS, 1998)

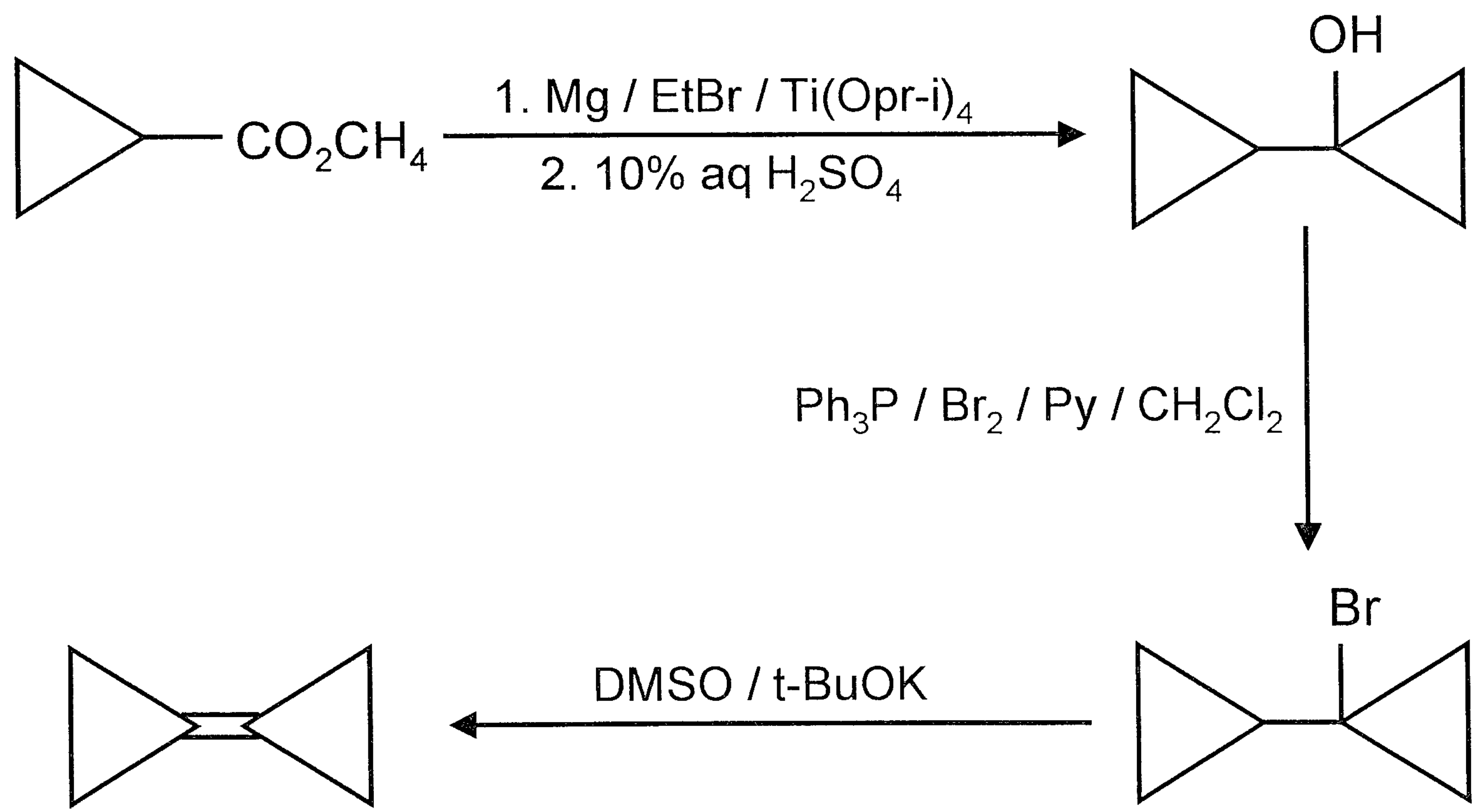
"The High Energy Density Material effort is based on a good science foundation. The work is well focused ... The overall approach from initial modeling, prototype synthesis, to production synthesis demonstrates excellent understanding of technology creation and delivery." -- USAF Scientific Advisory Board Quality Review (1999)

Approach to Developing HEDM Propellants

Employ a synergic blend of experimental and theoretical techniques derived from the disciplines of chemistry and physics

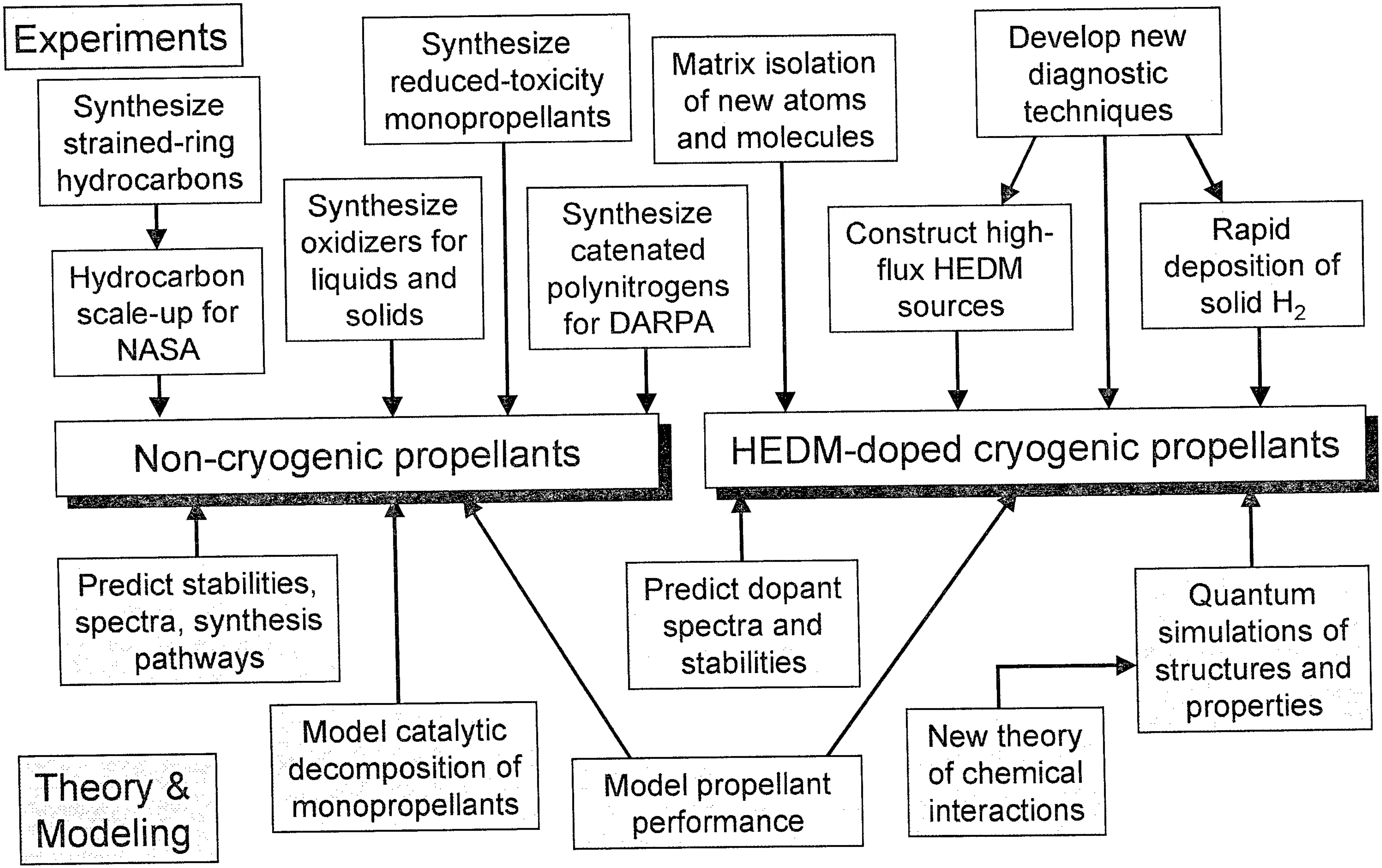


Synthesis of Bicyclopropylidene



AFRL innovations include eliminating the handling of a pyrophoric compound by *in situ* generation of first-step reagent

Overview of Current HEDM Research



Types of Research Contributing to Development of New Technologies

What scientists do:

- Basic research -- create new knowledge
- Applied research -- create new technologies

Science creates new technologies through the interaction of:

- Fundamental research -- done with little understanding of potential applications
- Strategic research -- resolve issues standing between knowledge and applications

	Fundamental	Strategic
Basic	Quantum mechanics (Einstein A and B coefficients)	Interaction of light with materials
Applied	Laser	Optical fibers

B. Richter, "The Role of Science in Our Society," *Physics Today*, Sept. 1995

Interplay of HEDM Research Components

Non-cryogenic HEDM propellants

	Fundamental	Strategic
Basic	Chemical principles (quantitative scale for Lewis acidity)	Laboratory-scale synthesis of new molecules
Applied	Pilot-plant synthesis and subscale tests of new ingredients	Prototype propulsion system for new propellants

Cryogenic HEDM propellants

	Fundamental	Strategic
Basic	Quantum mechanics (spectral theory of the chemical bond)	Synthesis and analysis of doped cryogenic HEDM solids
Applied	Combustion studies of cryogenic solid propellants	Prototype cryogenic HEDM solid propulsion system

Advanced Chemical Propellant Concepts

In its early years the program emphasized basic research on concepts with energy content exceeding 15 MJ/kg (nominally equivalent to about 500 seconds propellant specific impulse):

- Novel forms of matter -- tetrahydrogen, condensed triplet helium, metallic hydrogen
- Excited metastable molecules -- high-spin diatomics, ion-pair states
- Ionic species -- dications, rare-gas-hydride ions

Several factors have contributed to a significant redirecting of the program in recent years:

- Research results -- many "revolutionary" concepts pruned
- Impatience with long-term, high-risk research
- Desire for near-term payoffs -- "filling the bucket"
- Push for relevance to specific AF missions and requirements
- Decreased AF financial support

Current AFRL HEDM Research Areas

1st [illegible]

- Discovery, lab-scale synthesis, and pilot-plant development of strained-ring hydrocarbon fuel candidates
- Discovery and synthesis of novel oxidizers and monopropellant candidates
- Development of analytical and theoretical methods for analyzing seeded cryogenic HEDM solids
- Development of techniques for the production of seeded cryogenic HEDM solids
- Identification and testing of robust, high-flux sources of HEDM dopants to be used in codepositions with hydrogen

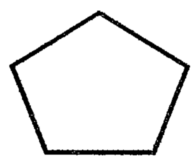
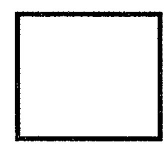
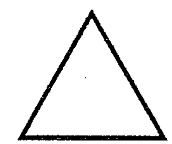
New Energetic Hydrocarbon Fuels: Challenges and Payoffs

Developing hydrocarbon fuels with increased energy contents

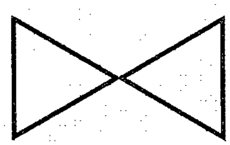
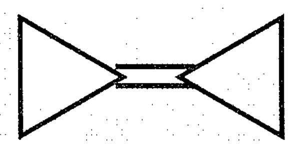
<u>The effect of unsaturation:</u>

	$H_3C{-}CH_3$	$H_2C{=}CH_2$	$HC{\equiv}CH$
ΔH_f (kcal/mol)	-4.9	+6.3	+27.0

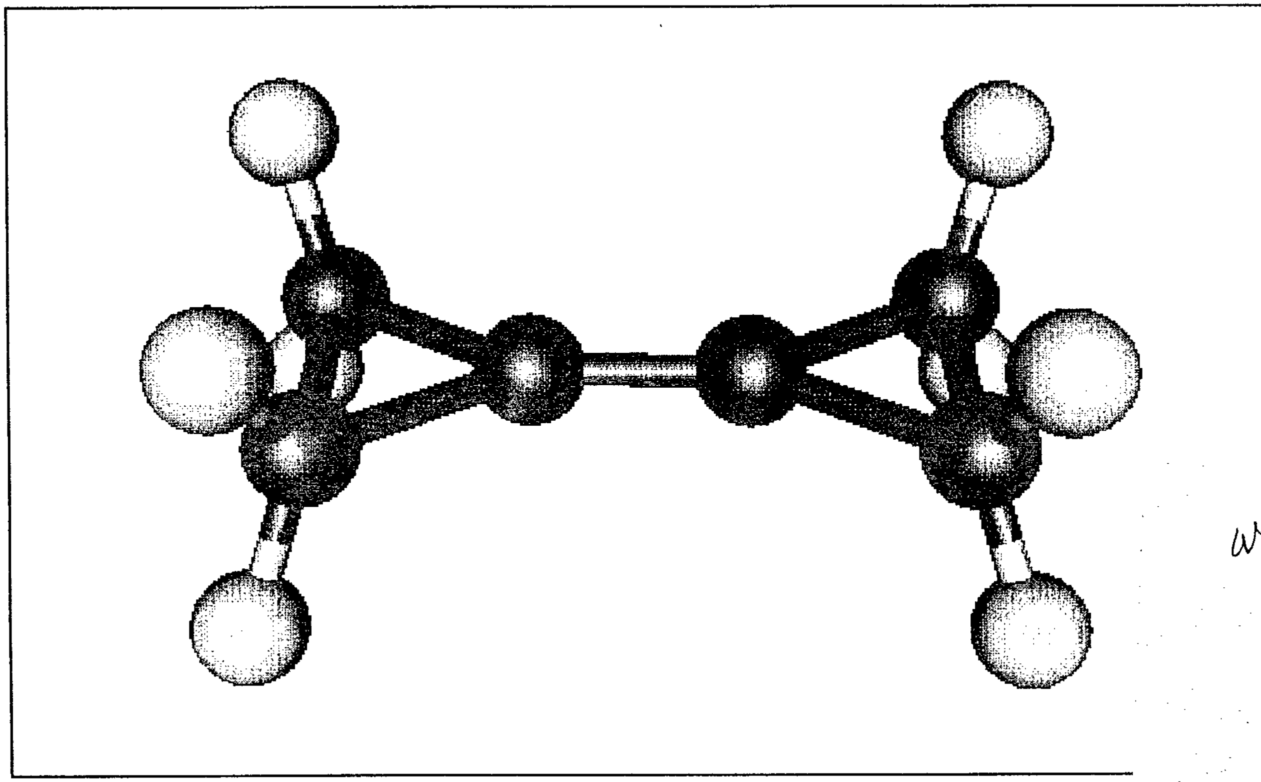
<u>The effect of strain:</u>

			
	cyclopentane	cyclobutane	cyclopropane
ΔH_f (kcal/mol)	-18.4	+6.8	+12.7

<u>Selected candidate HEDM fuels:</u>

			$HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$
	spiropentane	bicyclopropylidene	1,5-hexadiyne
Isp (sec; RP-1 = 299)	311	313	312

A New Energetic Hydrocarbon Fuel: Bicyclopropylidene



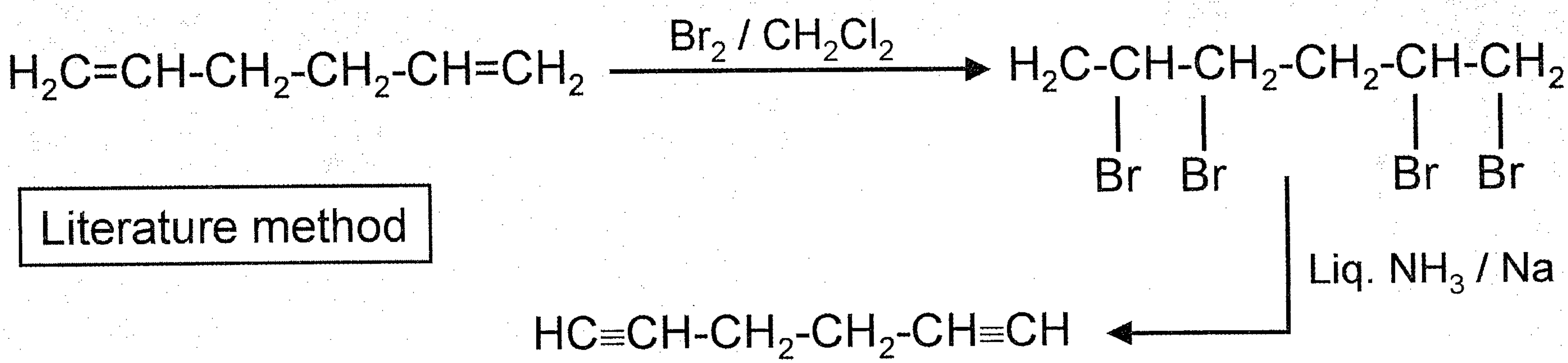
What is Isp threshold for ITAR?

<u>Synthesis was developed, optimized, and scaled up at AFRL</u>

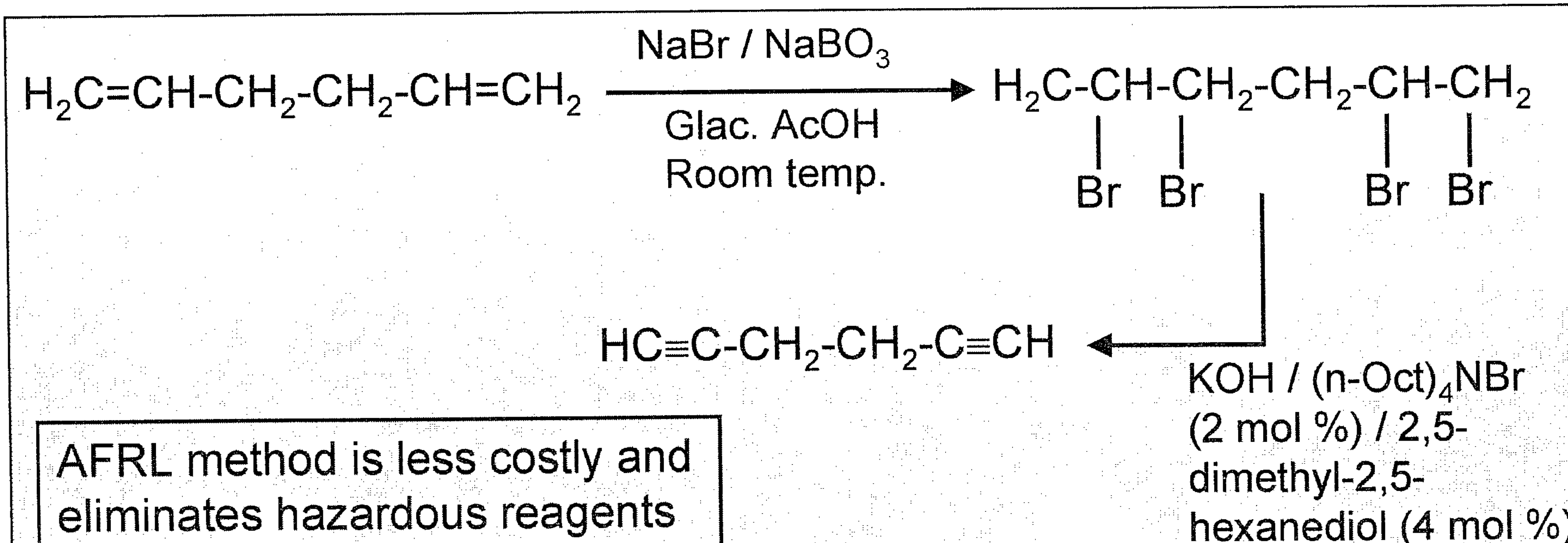
- Predicted specific impulse (with LOX) is 313 sec; Isp of RP-1 is 299 sec
- Would enable about 1500 lbs. more payload

on what launch system?

Synthesis of 1,5-Hexadiyne

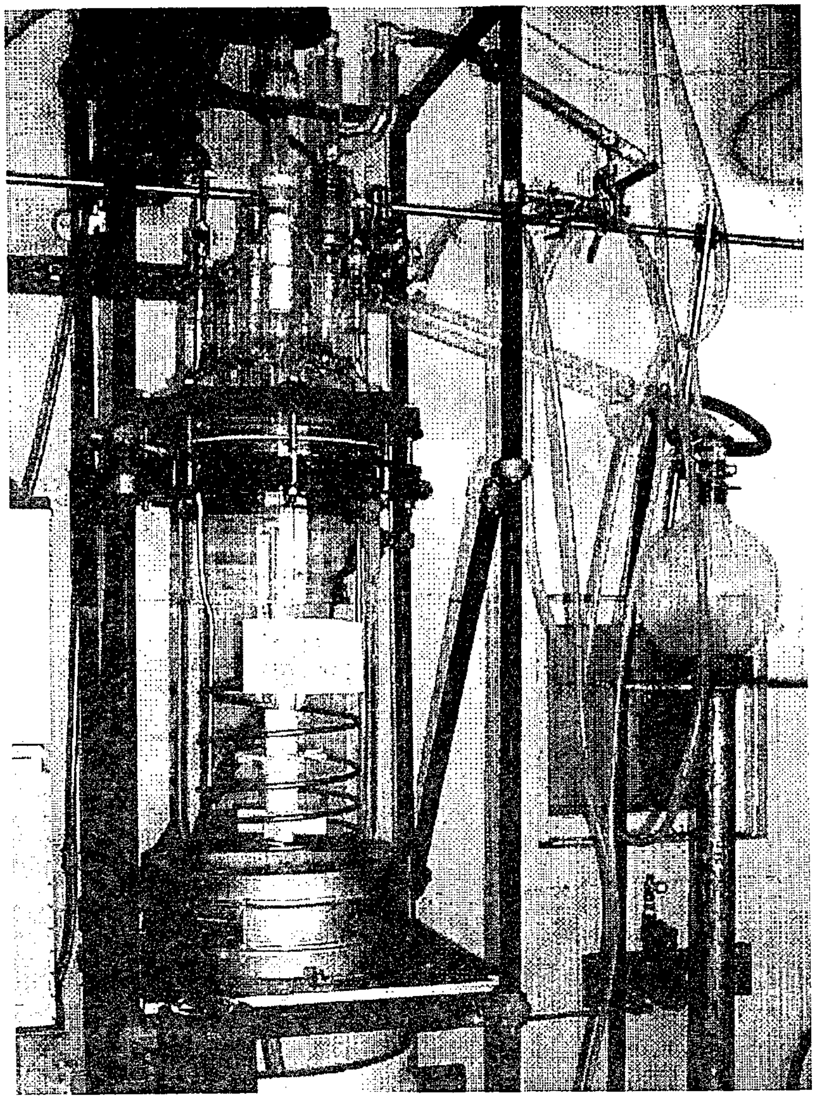


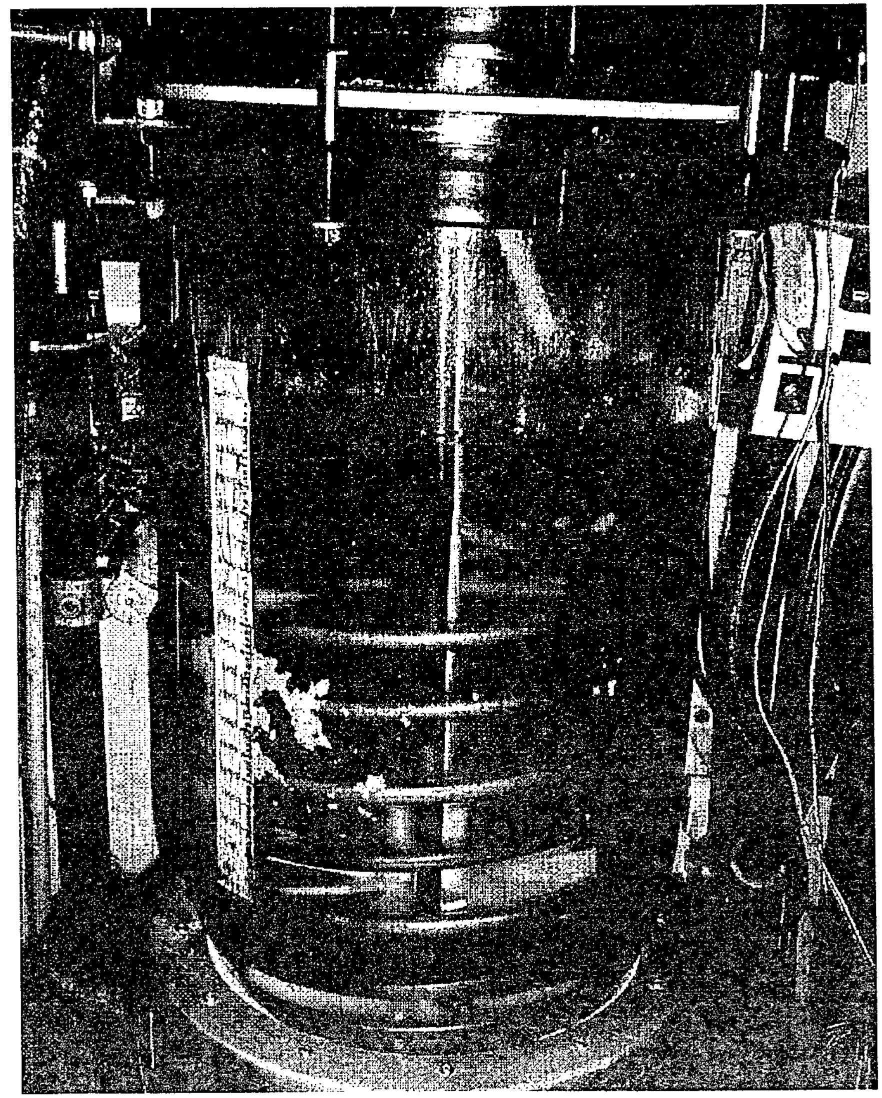
Literature method



AFRL method is less costly and eliminates hazardous reagents

Kilogram-Scale Synthesis of Bicyclopropylidene





New Energetic Oxidizers and Monopropellants: The Challenge

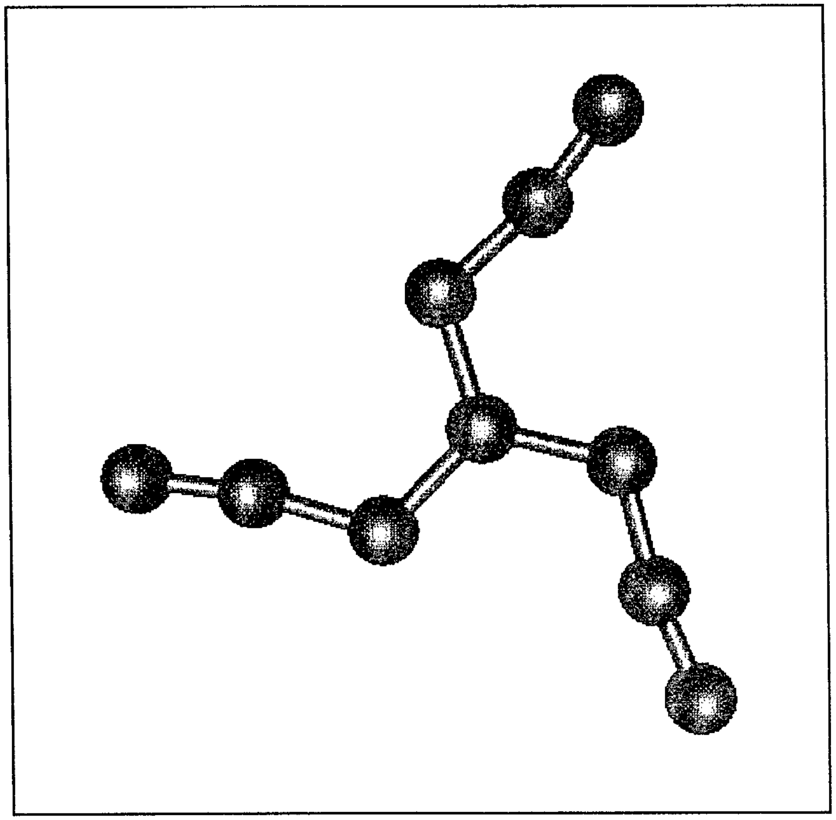
Synthesizing new materials at the limits of chemical stability

Caution! The azido compounds described in this study are highly shock sensitive and powerful explosives. These compounds should be handled only on a millimolar scale using appropriate safety precautions, i.e., face shields, gloves, protective jackets, and safety shields.

Immediately after weighing, the solid detonated sharply destroying the glass apparatus. The solids dissolved in the filtrate were not isolated. Subsequent syntheses were performed on a smaller scale (<15 mg) in an NMR tube fitted with a J. Young valve. Although five synthetic runs consistently resulted in the destruction of the apparatus, the identity of the salt was verified in one case by low-temperature Raman spectroscopy of a few isolated crystals remaining in the upper part of the tube after an explosion.

The resulting salts are very powerful explosives. Although their sensitivity is too high for practical applications, these compounds represent a new class of high-energy density materials and demonstrate that endothermicities as high as 1 kcal g^{-1} are achievable for ionic solids.

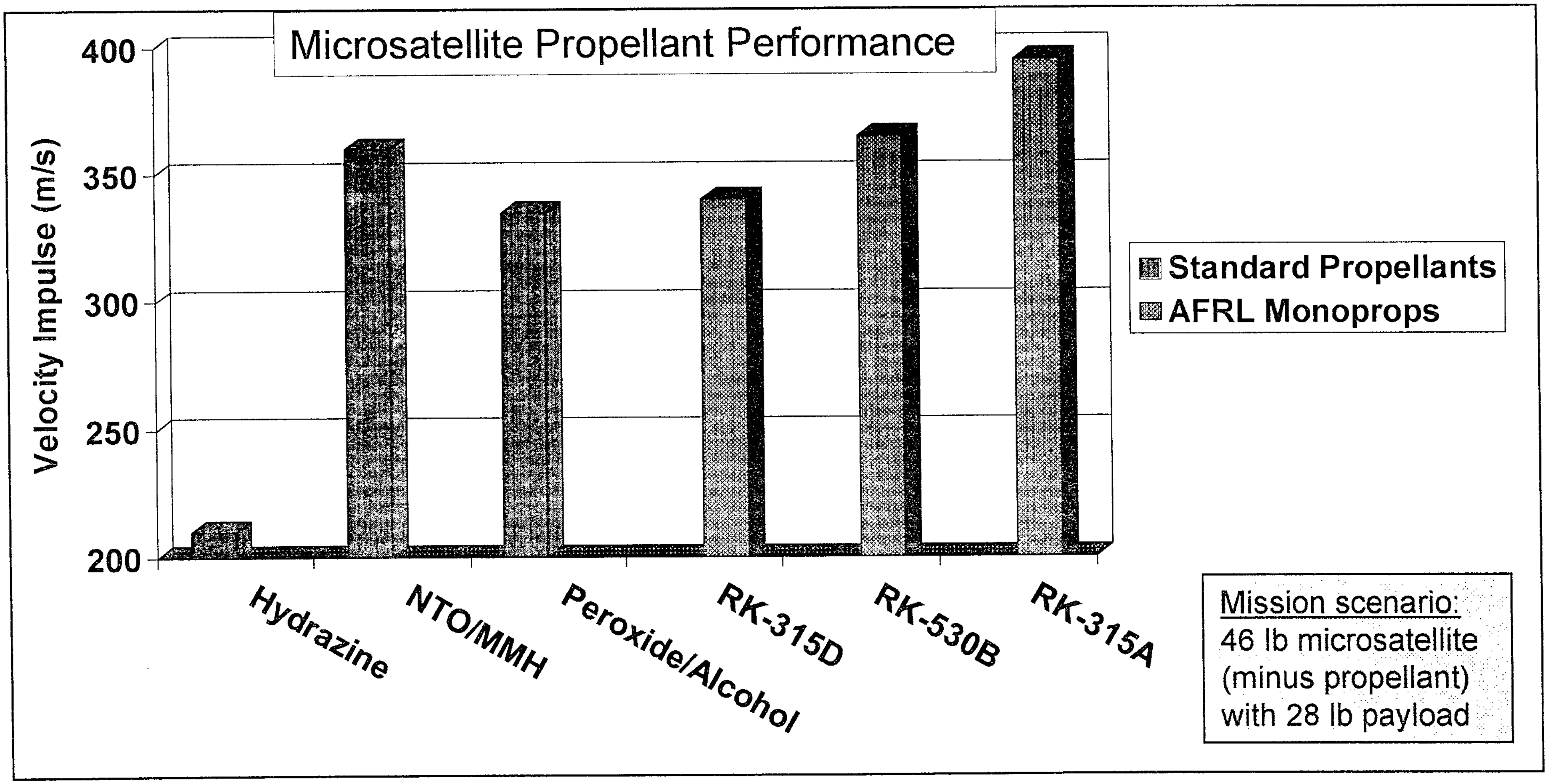
From Petrie, Sheehy, Boatz, Rasul, Prakash, Olah, and Christe, JACS 119 (1997) 8802



The extremely energetic triazidocarbenium cation, synthesized at AFRL

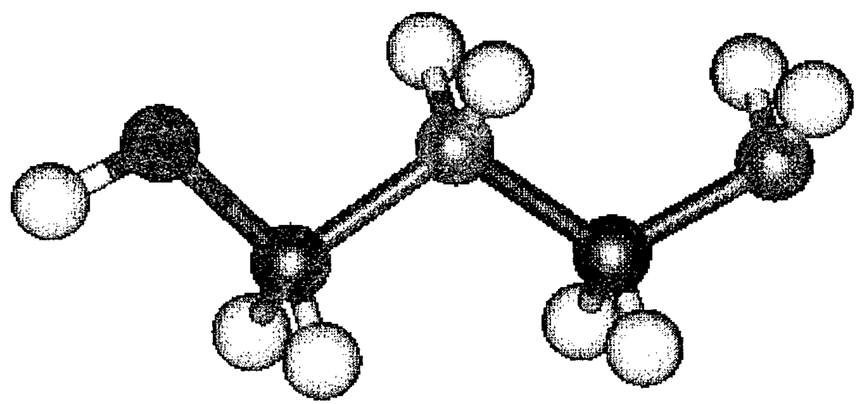
New Energetic Monopropellants: Payoffs

The performance of new advanced monopropellants can dwarf that of hydrazine, and can significantly exceed even bipropellant systems



New Families of High-Performance Reduced-Toxicity Monopropellants

Hydrazine, the current state-of-the-art monopropellant, is carcinogenic, dermally toxic, highly flammable, and has low energy density



The energetic hydroxyethylhydrazinium cation, synthesized, used in propellant formulations, and tested at AFRL

The nitrate, dinitrate, perchlorate, diperchlorate, and dinitramide salts of HEH may yield monopropellants that are superior to hydrazine:

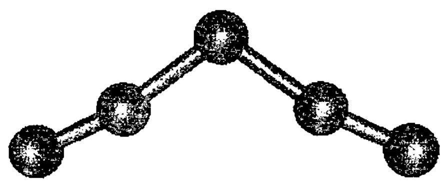
* 50% denser   * 25% higher Isp   * Much less toxic

Polynitrogen Synthesis

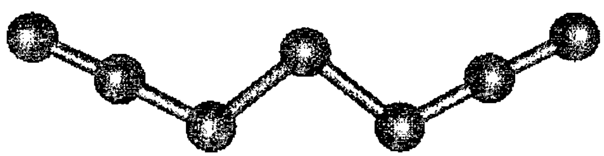
- Only two catenated polynitrogen compounds were known that could be prepared "in bulk:"
  - ⇒ N_2, long known but first isolated in pure form in 1772, independently by Rutherford, Scheele, and Cavendish
  - ⇒ Azide, N_3^-, discovered in 1890 by Curtius
- The absence of any other such compounds suggested that novel methods would be needed, and problems may be encountered along the way

> *"But there are men for whom the unattainable has a special attraction. Their ambitions and fantasies are strong enough to brush aside the doubts which more cautious men might have. At best such men are regarded as eccentric; at worst, mad ..."*
>
> \- *Walt Unsworth,* Everest

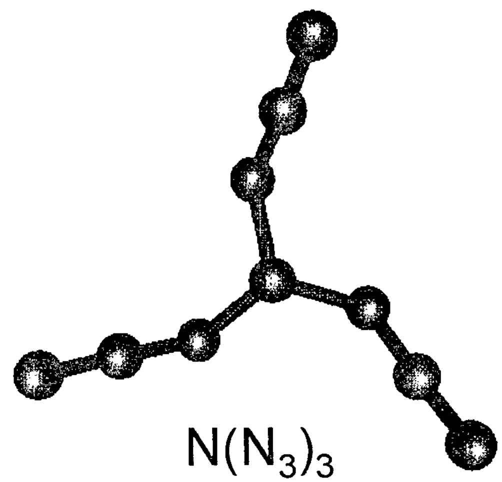
Catenated Polynitrogen Compounds



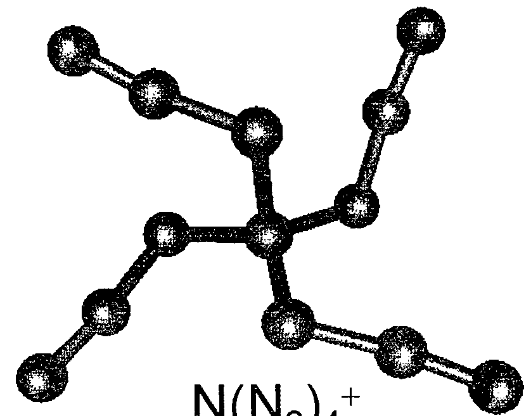
N_5^+



$N(N_3)_2^-$



$N(N_3)_3$



$N(N_3)_4^+$

These compounds have high calculated energy densities:

$N(N_3)_2^-$	ΔH_f = 170 kcal/mol	88 kcal per N_3 group
$N(N_3)_3$	ΔH_f = 306 kcal/mol	102 kcal per N_3 group
$N(N_3)_4^+$,	ΔH_f = 610 kcal/mol	153 kcal per N_3 group

New Energetic All-Nitrogen Compound

From *Chemical and Engineering News*, 25 Jan 99

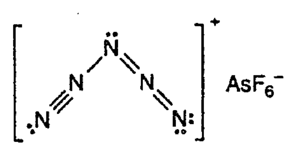
news of the week

N_5^+ CATION MAKES EXPLOSIVE DEBUT

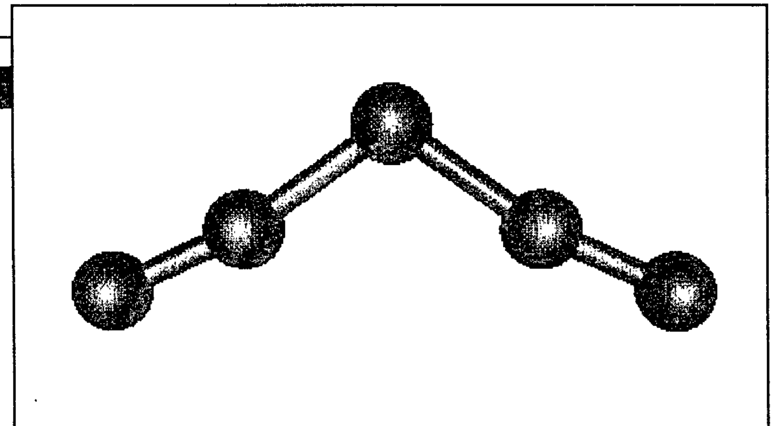
High-energy ion is first new all-nitrogen species in 100 years

It wasn't in his abstract, but Karl O. Christe, a chemist who studies high-energy materials at the Air Force Research Laboratory at Edwards Air Force Base in California, had a little something extra to offer last week in his plenary presentation at the American Chemical Society's Winter Fluorine Conference in St. Petersburg Beach, Fla. Along with colleague William W. Wilson, Christe has synthesized and characterized a salt containing the N_5^+ cation. The cation is the first new all-nitrogen species to be synthesized in isolable quantities in more than a century, and only the third ever to be produced.

Although species that contain only ni-



taking," says Gary J. Schrobilgen, a professor of chemistry at McMaster University, Hamilton, Ontario. "This synthesis could only be done in a very few laboratories in the world, and certainly Christe's is one of them." The work is supported by the Air Force Research Laboratory's propulsion directorate as well as by the Defense Advanced Research Projects Agency and the

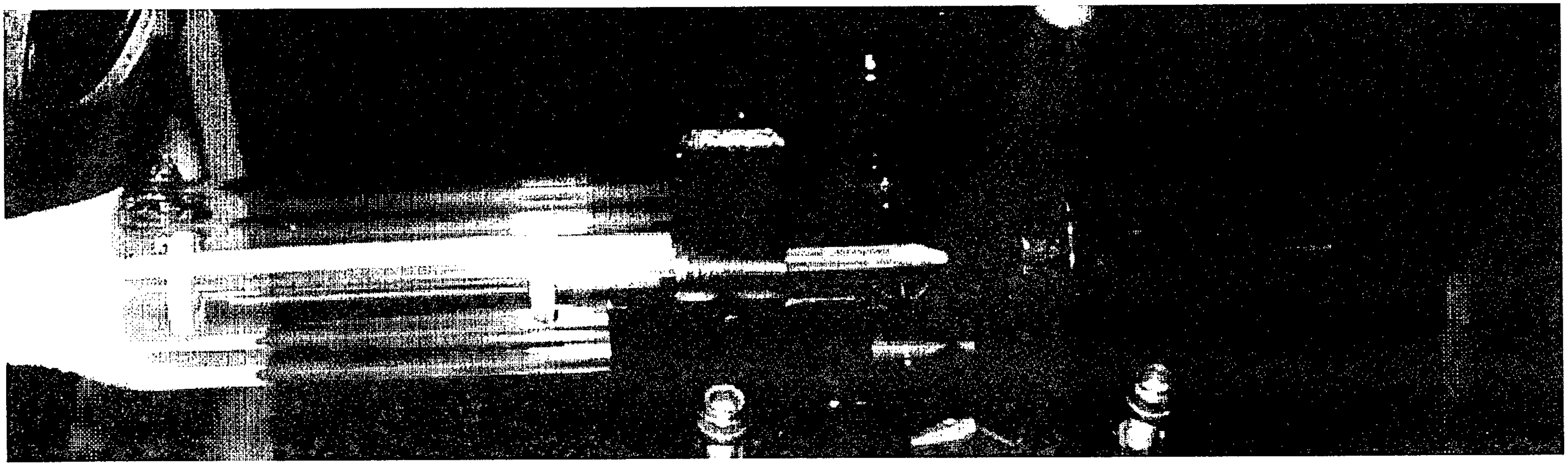


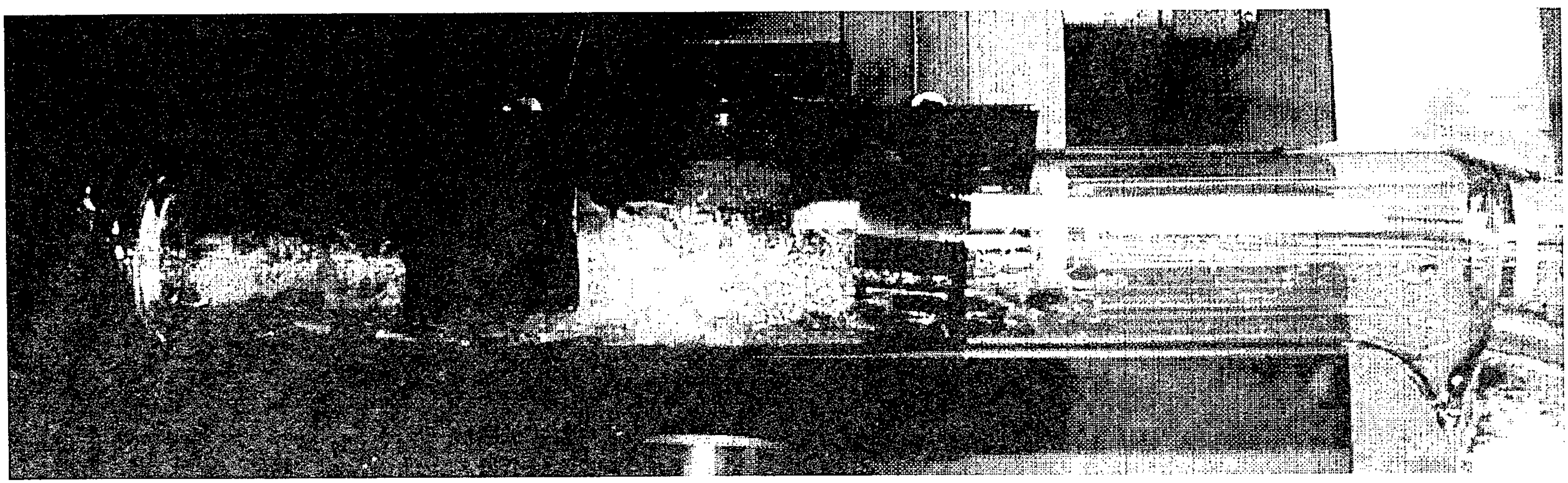
be theoretical chemists who are initially most interested in the new cation. "It's going to be of incredible interest to theoreticians who, perhaps, thought that compounds like this would be too unstable to isolate at all," Strauss says.

The salt is surprisingly stable, considering its huge calculated positive heat of formation of more than 350 kcal per mol, Christe points out. Vibrational spectroscopy and theoretical calculations by his coworkers Jeffrey A. Sheehy and Jerry A. Boatz show the cation to have a V shape in which resonance structures increase its stability.

Christe and his group envision other N_5^+ salts—such as $N_5^+SbF_6^-$—that might have even more thermal stability. They also would like to use the cation to pre-

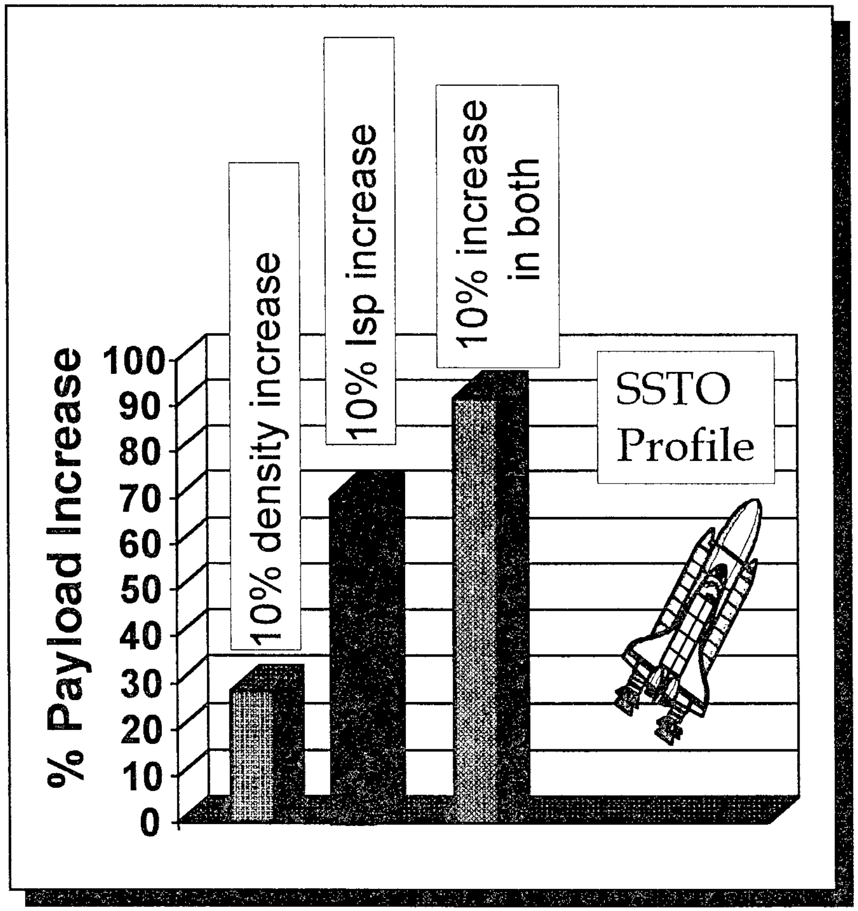
N_5^+ Salt in Low-Temperature Raman Spectrometer





Cryogenic Solid Propellants: Challenges and Payoffs

Use a solidified fuel or oxidizer as a storage medium for energetic additives, obtaining density and specific-impulse improvements

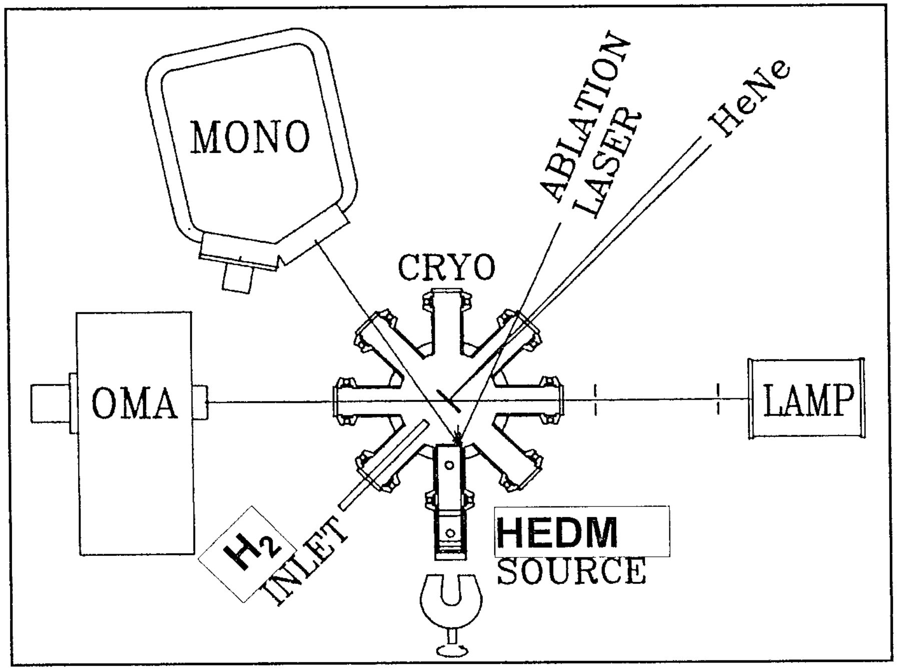


Large payload increases are achievable with modest density or specific impulse increases

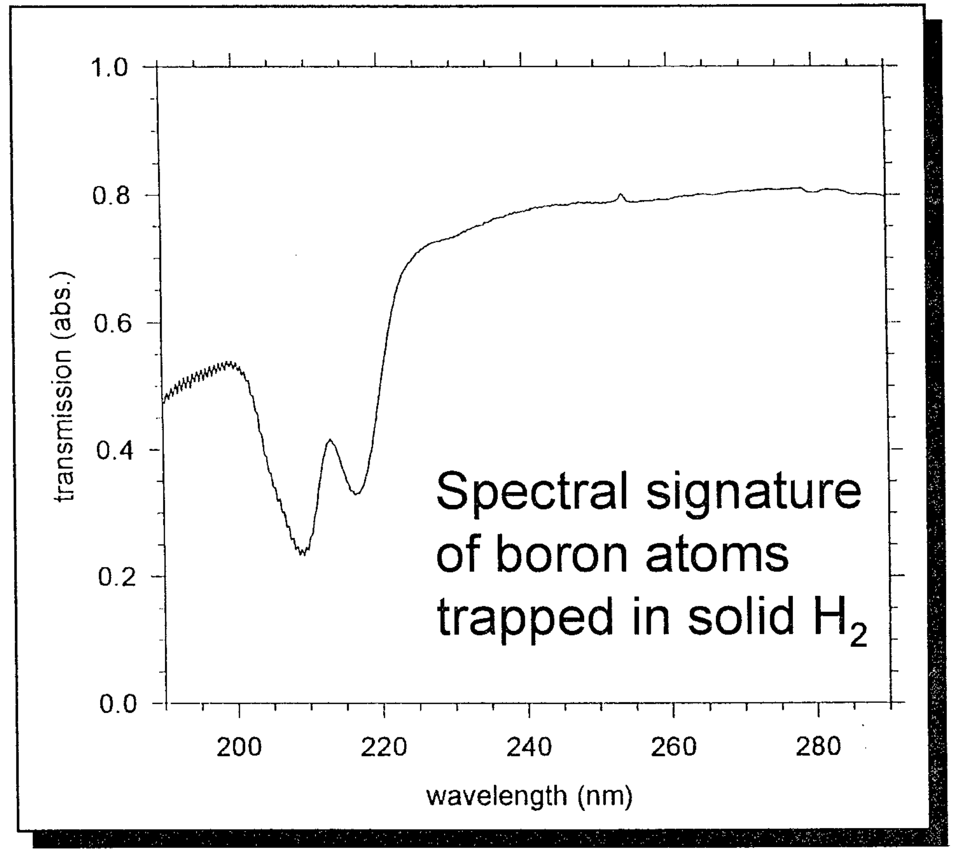
Our approach is to deposit energetic atomic and molecular species in solid hydrogen at liquid helium temperatures

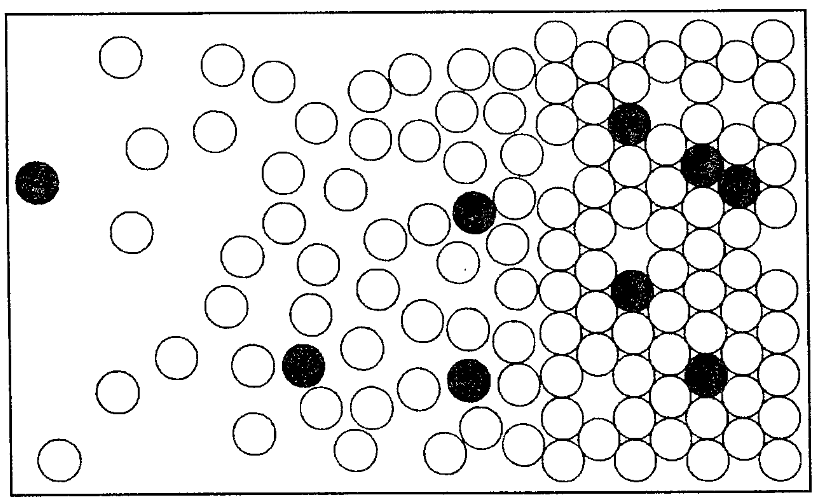
The propellants being developed by this method could increase payload capacity by 300%

Cryogenic Solid Propellants: Approach and Results



Schematic of the experiment

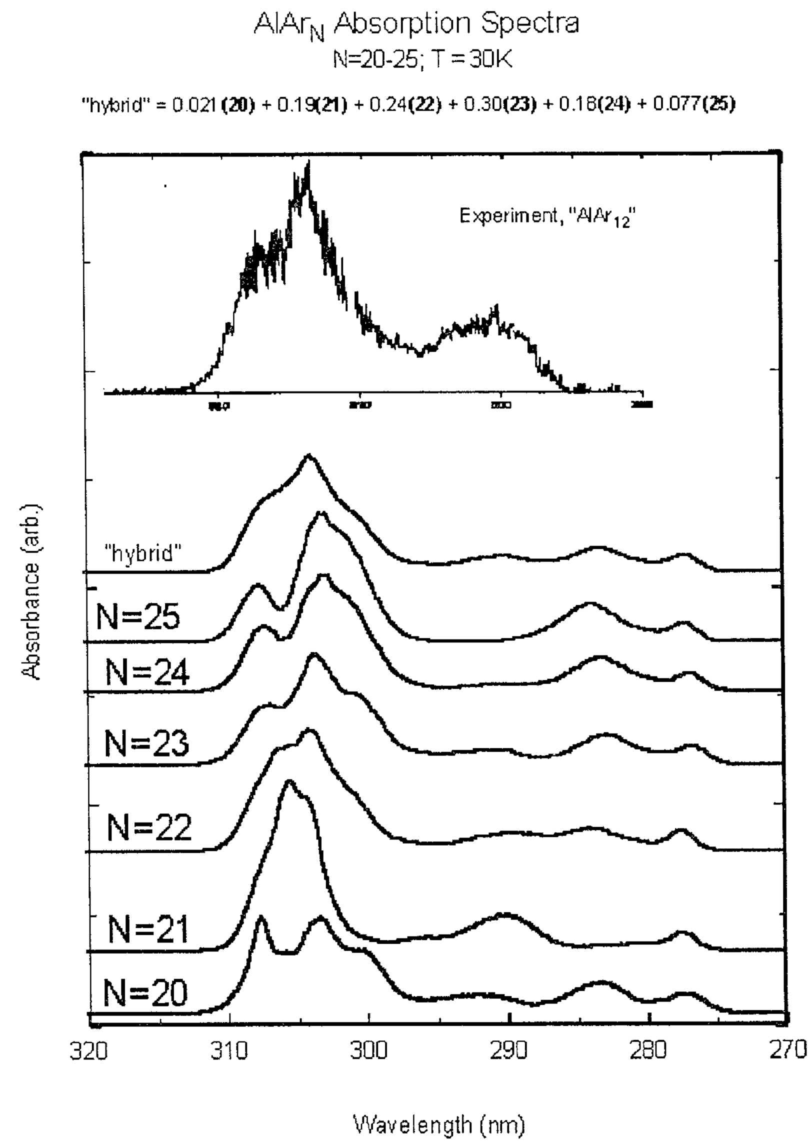




Schematic of the deposition process

Theoretical Methods for Analyzing Cryogenic HEDM Solids

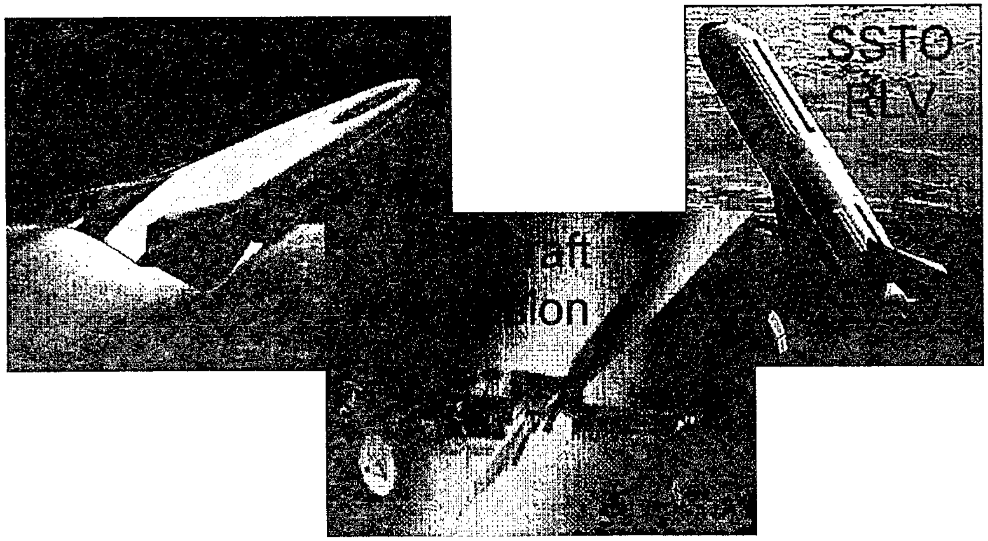
- The method has been applied to the analysis of the spectra and photo-fragmentation of solvated metal atoms
- Ab initio calculations are made of AlAr ground and excited-state diatomic potential curves
- Ground and excited state potential surfaces of clusters are constructed using the spectral theory approach
- Monte-Carlo simulations on these potential surfaces yield cluster structures and spectra
- Diffusion Monte-Carlo methods yield the ground-state wave function of a parent cluster
- Molecular dynamics simulations of photo-fragmentation patterns



Recent Accomplishments

Accomplishment	Impact
Pilot-plant synthesis of bicyclopropylidene and 1,5-hexadiyne	These compounds offer about 5% greater propellant Isp than the ubiquitous RP-1
Synthesized salts of the catenated polynitrogen N_5^+	The first of the long-sought, highly-energetic polynitrogens to ever be made
Energetic salts of 2-hydroxyethyl-hydrazine were synthesized and delivered for thruster testing	These compounds are denser, higher-performance, and reduced-toxicity alternatives to hydrazine
Developed a method of rapidly depositing gram-scale samples of HEDM-seeded solid H_2	Solid H_2 is 25% more dense than the commonly used LH2; doped solid H_2 gives Isp increases of as much as 25%
Designed and constructed an apparatus for characterizing HEDM dopant sources	Facilitates optimization of dopant sources
Developed a new theory of interactions in chemical systems	Permits accurate property predictions for condensed-phase chemical systems, including cryogenic HEDM propellants

High Energy Density Matter:
The Superpropellants of the Future Space Force

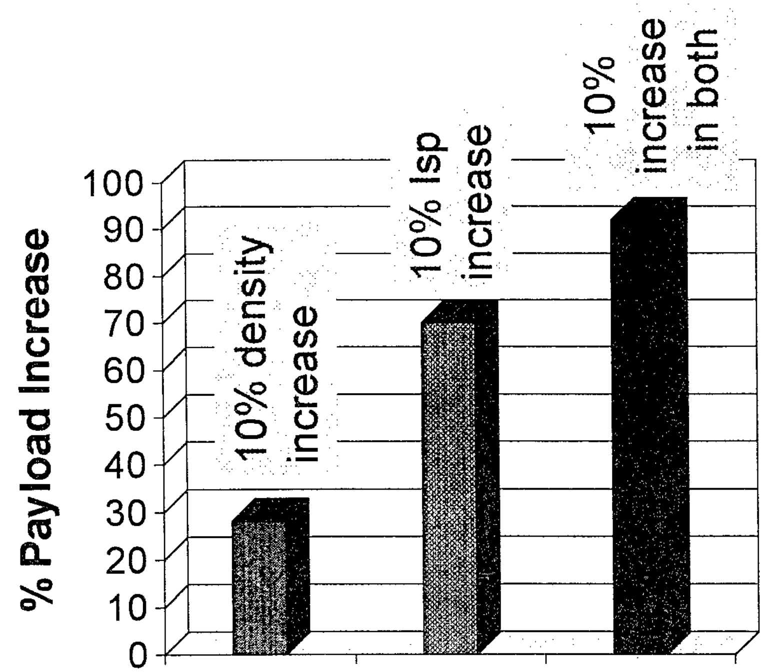


Discovering and developing new high energy density propellants that deliver as much as 50% greater performance

- Enables larger payloads, smaller vehicles, and lower launch costs
- Improves our capacity to access and exploit space

Several promising concepts are undergoing extensive synthesis, scale-up, and testing

- Strained-ring molecular systems as high energy density fuels and oxidizers
- Unique inorganic molecular systems as high energy density oxidizers and monopropellants
- Cryogenic stabilization of energetic species in fuels or oxidizers



Activities Supporting HEDM Research

- Thermal stability, friction sensitivity, and impact sensitivity testing of candidate HEDM propellants and ingredients
- Card-gap testing to determine explosive classification of candidate HEDM propellants and ingredients
- Developing propellant formulations using HEDM oxidizer and monopropellant ingredients
- Test firings of new monopropellant formulations using a hydrazine-type thruster
- Equipment and personnel support of pilot-plant liquid hydrocarbon fuel synthesis